

The University of Chicago

A STUDY OF
THE ELECTRONEGATIVITIES OF
ORGANIC RADICALS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1935

By
HERMAN PINES

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OBJECT OF THE WORK

The object of this work was to determine:

- 1) How the electronegativity of the phenyl radical is affected by the introduction of various ortho, meta, and para substituents.
- 2) The order of electronegativity of the ortho, meta, and para chlorobenzyl radicals.
- 3) How the electronegativity of the meta 1,1,1-trifluorotolyl radical compares with that of the phenyl and metachlorophenyl radicals.
- 4) The effect of variation in solvent and hydrolytic agent upon the order of electronegativity of organic radicals.

INTRODUCTION AND METHOD OF ESTABLISHING THE RELATIVE ELECTRONEGATIVITY

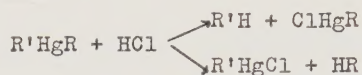
Kharasch and coworkers¹ have studied the electronegativity of organic radicals with the purpose of using the information in the interpretation of organic reactions.

Before the work of Kharasch and his coworkers appeared, the terms "positive" and "negative" radical with reference to organic radicals were too indefinite to be of any use. A single term "relative electronegativity" has been proposed by Kharasch. By "electronegativity" of a radical is meant the affinity of that radical for the pair of valence electrons. The attraction of the

¹Kharasch and Grafflin, Science, 58, 1510 (1923); Kharasch and Grafflin, J. Am. Chem. Soc., 47, 1948 (1925); Kharasch and Marker, J. Am. Chem. Soc., 48, 3130 (1926); Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1933).

radical for the pair of valence electrons is a function of the electronic structure of the molecule and thus arises the difference of electronegativity of organic radicals.

The method of establishing the relative electronegativity of organic radicals has been described by Kharasch and Marker.² This method depends upon the fact that when hydrogen chloride is added to an unsymmetrical mercury compound, one of the following reactions takes place:



The group which presumably first dissociates from the mercury and then combines with the hydrogen ion in solution to form the hydrocarbon R'H is defined as the more electronegative of the two radicals; that is, it has the greater attraction for electrons.

If the radicals R and R' differ widely in their relative electronegativity, the decomposition of R'HgR proceeds quantitatively in one direction. If there is a small difference in the relative electronegativity of the radicals R' and R, the decomposition with hydrogen chloride will give two products, but the substance containing the less electronegative radical always constitutes the greater proportion of the mixture of RHgCl and R'HgCl.

By suitably varying the substituents R' and R, the relative order to electronegativity of a considerable number of organic radicals has been determined. A table of relative electronegativities of organic radicals was arranged by Kharasch and Marker, and Kharasch and Flenner.

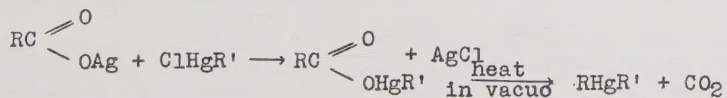
²Kharasch and Marker, J. Am. Chem. Soc., 48, 3130 (1926).

HISTORICAL PART

Before the work of Kharasch and his coworkers, the only unsymmetrical organo-mercury compounds described in the literature were those recorded by Hilpert and Grüttner.³ They specifically stated, however, that in order to obtain these compounds it was necessary to condense the materials in a definite order. Thus they succeeded in preparing mercury phenyl ethyl by treating ethyl mercuric chloride with phenyl magnesium bromide, but were unable to obtain the desired product if the order was reversed. They stated that in some cases the unsymmetrical compound could not be prepared at all, for example, the treatment of ethyl magnesium bromide with naphthyl mercuric chloride resulted in the formation of mercury diethyl instead of mercury ethyl naphthyl.

Kharasch and Marker found that Hilpert and Grüttner's failure was due to use of too large an excess of Grignard reagent and to their heating of the reaction mixture. When these two factors were controlled, it was possible to prepare many unsymmetrical organo-mercury compounds by means of the Grignard reagent.

Another method for the preparation of unsymmetrical organo-mercury compounds, which could not be prepared by the method discussed above, has been described by Kharasch and Grafflin.⁴ This method depends upon the elimination of carbon dioxide from a molecule of the type $\text{RC} \begin{smallmatrix} \text{=O} \\ \text{OHgR}' \end{smallmatrix}$ where $\text{RC} \begin{smallmatrix} \text{=O} \\ \text{OH} \end{smallmatrix}$ represents an acid which loses carbon dioxide readily. The general reaction may be represented by the following equation:

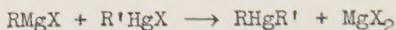


³Hilpert and Grüttner, Ber., 48, 908 (1915).

⁴Kharasch and Grafflin, J. Am. Chem. Soc., 47, 1948 (1925).

PROOF OF THE STRUCTURE OF RHgR'

The method of preparing the unsymmetrical mercury compounds used in this work may be represented as follows:



These unsymmetrical compounds are in some cases heavy viscous oils with a characteristic, nauseating odor. In many cases they are solid, but always of lower melting point than the corresponding symmetrical compounds.

The proof of the structure of the unsymmetrical organo-mercury compounds depends upon three criteria: (1) an analysis for mercury; (2) the reaction of the compound with mercuric chloride; (3) the reaction with hydrogen chloride.

As carried out in the laboratory the character of the unsymmetrical compound is divided into three portions:

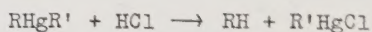
The first portion is analyzed for mercury.

The second portion is decomposed with mercuric chloride, a reaction which proceeds quantitatively yielding equimolar quantities of the two organo-mercuric halides,



which are separated and identified.

The third portion is decomposed with a solution of hydrogen chloride in ethanol. This reaction results in the formation of either an organo-mercuric halide and a hydrocarbon, or a mixture of both organo-mercuric halides and two hydrocarbons, depending on the relative electronegativity of the radicals R and R'. The reaction proceeds thus:



if the two radicals lie far apart in the "Table of Electronegativities."⁵ In this equation R is much more electronegative than R'.

⁵Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932).

However, if these electronegativities are close together, $R'H$ and $RHgCl$ also are formed.

A correct mercury content and the decomposition by mercuric chloride indicate only that the substance in question is either the unsymmetrical compound or an equimolecular mixture of the two symmetrical compounds. The latter possibility can often be eliminated by a comparison of the physical and chemical properties of the substance with those of an equimolecular mixture of the two symmetrical substances. In any case, the decomposition with hydrogen chloride is the final test. An amount of $RHgR'$ corresponding to its formula weight can yield as high as one formula weight of $R'HgCl$. If instead of $RHgR'$, however, we have an equimolar mixture of $RHgR$ and $R'HgR'$, the reaction with hydrogen chloride can yield only fifty per cent of each organo-mercury compound ($RHgCl$ and $R'HgCl$) since half of each molecule must form the corresponding hydrocarbon.

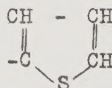
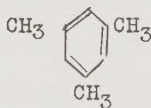
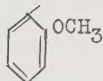
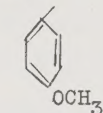
An objection could be raised that where analysis shows the presence of two different radicals, to obtain (by the use of hydrogen chloride), a single reaction product ($R'H$) is not conclusive proof that the reacting substance is an unsymmetrical mercurial, $RHgR'$. This same result might be obtained from an equimolecular mixture of $R'HgR'$ and $RHgR$, if the rate of reaction of the former compound was much greater than that of the latter compound. However, the decomposition by hydrogen chloride of an equimolecular mixture of mercury diethyl and mercury diphenyl has shown this objection to be unfounded. The mixture in question gives nearly equimolecular amounts of phenyl mercuric chloride and ethyl mercuric chloride in sharp contrast to the unsymmetrical phenyl mercury ethyl which yields ethyl mercuric chloride alone in spite of the fact that phenyl mercuric chloride is much less

soluble in ether than ethyl mercuric chloride, and hence would be the expected reaction product if relative solubility rather than relative electronegativity was the important influence guiding the course of the reaction.

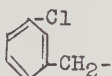
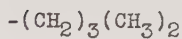
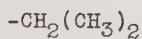
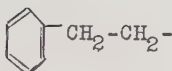
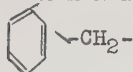
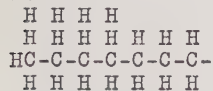
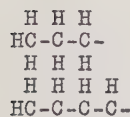
DISCUSSION OF THE TABLE OF ELECTRONEGATIVITIES

Unsymmetrical organo-mercury compounds decompose when treated with hydrogen chloride. The radical which dissociates more readily from the mercury and then combines with the hydrogen ion in solution is considered to be the more electronegative. Using this criterion the organic radicals studied by Kharasch and Marker and Kharasch and Flenner⁶ were arranged in the following table with the electronegativity of the radicals diminishing from the top of the table downward.

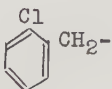
(CN)



⁶Kharasch and Flenner, J. Am. Chem. Soc., 54, 678 (1932).



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One of the conclusions which could be drawn from the table of electronegativities is that direct substitution reduces the electronegativity of the phenyl radical. Chlorophenyls are less electronegative than phenyl. The work by Kharasch and Legault⁸ on mono- and di-substituted phenyl radical supports this conclusion.

SIGNIFICANCE OF THE TABLE OF ELECTRONEGATIVITIES
IN THE PREDICTION AND INTERPRETATION
OF ORGANIC REACTIONS

The postulates involved in the theory of relative electronegativity are these:

- 1) That organic radicals possess varying degrees of electronegativity.
- 2) That the nature of the carbon-carbon bond varies in accordance with the relative electronegativities of the radicals which it joins.

In the present state of our knowledge of the physical configuration of the organic radical, it is impossible to predict with mathematical exactitude just what strains may be set up or how the degree of electronegativity may be affected by substitutions in carbon chains. Nevertheless, even though such a prediction may occasionally fail, once the table of relative electronegativity is given, it is possible to predict with precision the nature and the degree of stability of the bond which will be formed by their union.

⁸Kharasch and Legault, Unpublished Master's thesis, University of Maryland.

DISCUSSIONS OF RESULTS AND CONCLUSIONS

1. Effect of Solvents and Hydrolytic Agents Upon the Splitting of Unsymmetrical Organo-Mercury Compound

The table of electronegativity of organic radicals could have an application if it could be proven that the order of electronegativity is not affected by the type of solvent used, by the hydrolytic agent used to accomplish the reaction and by the relative solubility of the possible reaction products.

To show that the order of electronegativity is not changed by solvents and by the hydrolytic agents used, mercury phenyl ethyl was decomposed with a solution of hydrogen chloride, hydrogen bromide and hydrogen iodide in alcohol benzene and glacial acetic acid.

The melting points of the products obtained from the decomposition of mercury phenyl ethyl are given in the following table.

	<u>Decomposing Agent</u>		
	HCl	HBr	HI
Solvents used.....			
Glacial acetic acid.....	---	189°	181°
Ethanol.....	192°	189°	---
Benzene.....	---	189°	175°

The melting points of the end products are those of the corresponding ethyl mercury halides.⁹

From the foregoing results it is seen that the phenyl radical is more electronegative than the ethyl radical regardless of whether hydrogen chloride, bromide or iodide is used as the

⁹Melting point of ethyl mercuric chloride 192°
 iodide 182°
 phenyl mercuric chloride 251°
 bromide 276°
 iodide 266°

cleavage agent. Solvents and relative solubilities of the reaction products similarly do not affect the order of the electronegativity of the radicals.

2. The Effect of Substitution in the Benzene Ring

The relative electronegativity of phenyl and substituted phenyl radicals (fluoro, chloro and bromo phenyls) was investigated. It was found that in all but one of the cases direct substitution reduces the electronegativity of the phenyl radical. This observation is in agreement with the results obtained by Kharasch and Flenner.¹⁰

The results are summarized in the following table, which lists the unsymmetrical mercury compounds studied and the percentage of phenyl and substituted phenyl mercuric chloride obtained from the cleavage with hydrogen chloride.

Unsymmetrical Mercury Com- pound Investi- gated	Cleavage Agent: HCl	
	Substituted Phenyl Mercuric Chloride Obtained %*	Phenyl Mercuric Chloride Ob- tained %*
m-FC ₆ H ₄ HgC ₆ H ₅	100	0
p-FC ₆ H ₄ HgC ₆ H ₅	20	80
	20	80
	43	57
p-ClC ₆ H ₄ HgC ₆ H ₅	70	30
	78	22
o-BrC ₆ H ₄ HgC ₆ H ₅	100	0
m-BrC ₆ H ₄ HgC ₆ H ₅	100	0
p-BrC ₆ H ₄ HgC ₆ H ₅	76	24
	74	26

*The percentage was based on the mercury analysis of the product obtained from the cleavage with hydrogen chloride.

¹⁰Kharasch and Flenner, J. Am. Chem. Soc., 54, 684 (1932).

3. The Effect of Substitution in an Aromatic Side Chain

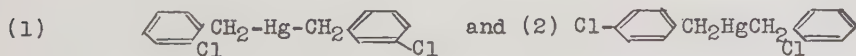
Kharasch and Flenner have found that the meta-tolyl radical is more electronegative than the phenyl and meta-chloro phenyl radicals. In order to study the effect of substitution in the side chains, upon the relative electronegativity of radicals, meta-1,1,1 trifluorotolyl radical was compared with phenyl and meta-chlorophenyl radical.

The results summarized below show that direct substitution in an aromatic side chain lowers the electronegativity of the radical.

<u>Cleavage Agent: HCl</u>		
Unsymmetrical Mercury Compound Investigated	Meta-1,1,1 trifluorotolyl Mercuric Chloride Obtained %	Other Compounds Obtained %
		Phenyl mercuric chloride
m-CF ₃ C ₆ H ₄ HgC ₆ H ₅	91	9
		m-Chlorophenyl mercuric chloride
m-CH ₃ C ₆ H ₄ MgC ₆ H ₄ Clm	65 70	35 30

4. Relative Electronegativity of Chlorobenzyls

A comparison was made of the relative electronegativity of ortho, meta and para chlorobenzyl radicals. The unsymmetrical chlorobenzyls are relatively stable and are not decomposed readily by alcoholic hydrogen chloride. The hydrogen chloride decomposition products of

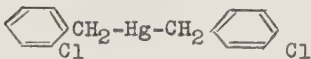
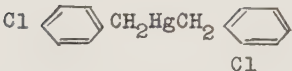


consisted in both cases of a mixture of the two chlorobenzyl

mercury chlorides, as is evident from the melting point and mercury analysis of the products of the split.

In the case of (1) the decomposition product consisted of an equimolal mixture of ortho-chlorobenzyl mercury chloride and of meta-chlorobenzyl mercury chloride. This was shown from the melting point of the cleavage product and the melting point of synthetic mixtures of ortho- and meta-chlorobenzyl mercury chlorides.

The results obtained are tabulated below:

Unsymmetrical Mercury Compound	Cleavage Agent: HCl M.P.
	87°
	99-110°

The melting points of the chlorobenzyl mercury chlorides are:

o-ClC ₆ H ₄ CH ₂ HgCl	M.P.	115° C.
m-ClC ₆ H ₄ CH ₂ HgCl	"	141° C.
p-ClC ₆ H ₄ CH ₂ HgCl	"	141° C.

EXPERIMENTAL PART

I. Analytical Methods Used for the Determination of Mercury

Three analytical methods were used for the determination of the mercury present in the organo-mercuric compounds.

1) The first method used was described by Kharasch and Flenner¹¹ as follows:

About 0.2 g. of sample is weighed into a 250 cc. Erlenmeyer flask, 20 cc. of glacial acetic acid added and then 3 cc. of

¹¹Kharasch and Flenner, J. Am. Chem. Soc., 54, 686 (1932).

bromine. After standing for about twelve to twenty-four hours, 5 cc. of hydrochloric acid is added and then zinc dust, in small amounts at a time, care being taken to add the zinc slowly so that the temperature may not rise above 40° . As soon as all the color of bromine has disappeared, a slight excess of zinc is added and the mixture allowed to react for about two hours or longer. A small amount of finely powdered silica gel (the silica gel is added to retain any colloidal mercury that may be present) is then added to the mixture and the supernatant liquid filtered through a Gooch crucible, the asbestos pad of which has been previously covered with silica gel. The residue remaining in the flask is washed by decantation until free from halogen, the washings being poured through the Gooch crucible. The asbestos pad is then removed from the crucible and added to the residue in the flask and any mercury adhering on the walls of the crucible is washed into the flask by dilute nitric acid. The combined residue is dissolved in 1-1 nitric acid and when completely dissolved, the potassium permanganate, ferrous sulfate and ferric alum are added in this order. The mercury is then titrated with potassium thiocyanate until the pink color persists.

It is important not to destroy the excess potassium permanganate with ferrous sulfate until just before the titration with potassium thiocyanate.

When titrating with potassium thiocyanate it is necessary in order to insure the proper end-point that a blank be run and the colors made to match. Due to the tendency of the color to fade, this blank must be made at the time of titration.

2) The second analytical method used was the electrolytic method described for inorganic compounds by Smith,¹² and modified

¹²E. F. Smith, "Electro-Analysis," P. Blakiston's Son, Philadelphia, 1918, p. 99.

for use on organic compounds by Legault and Sprowls.¹³

A sample (about 0.4 g.) was weighed into an electrolytic beaker, 5 cc. of glacial acetic acid was added, and the mixture was warmed on the steam bath in order to dissolve the organic compound. Bromine (2 cc.) was then added to effect decomposition of the substance, and after the solution had been warmed on the steam bath and then allowed to stand for thirty minutes, 8 cc. of amylene was added to destroy the excess of bromine. The solution was neutralized by the addition of 85 cc. of 6.67 per cent sodium bicarbonate solution and 15 cc. of 10 per cent sodium carbonate solution, and acidified with 8 cc. of concentrated nitric acid. It was then electrolyzed for two hours by means of a current of 5.75 amperes. The temperature of the solution rose to 80° during the course of the reaction and remained there throughout the electrolysis. The mercury was deposited on a previously weighed, perforated, cylindrical, gold electrode. After completion of the electrolysis, the electrode was washed with water, alcohol and ether, dried in a desiccator over phosphorous pentoxide and weighed.

3) The third method of analysis for mercury was that described by Whitmore and Sobatzki:

About 0.1 g. of mercuribis compound or 0.2 g. of organo-mercuric halide, weighed accurately, is mixed with 1 g. of potassium iodide, 2 cc. of chloroform, 25 cc. of water and 25.00 cc. of approximately 0.1 N iodine solution in a 100 cc. Erlenmeyer flask attached to a reflux condenser by a ground joint. The flask is heated enough to cause the chloroform to reflux gently for fifteen to thirty minutes. During the refluxing, 25.00 cc. of the iodine solution used is titrated with accurately standardized sodium thiosulphate solution (approximately 0.05 N). The flask containing the reaction mixture is cooled, acidified with 2 drops of concentrated hydrochloric acid and titrated with the standard thiosulphate. The difference in the thiosulphate used here and with the blank iodine titration gives a measure of the C-Hg linkage

¹³Private communication.

present, each such linkage corresponding to two equivalents of iodine or thiosulphate.¹⁴

II. Preparation of Intermediate Compounds

1. Preparation of Fluorobromobenzene

The method used, that of G. Balz and G. Schiemann¹⁵ consists of heating bromophenyldiazonium boronfluoride, which decomposes to give boronfluoride and bromofluorobenzene. The procedure was as follows:

To 30 g. of bromo-aniline was added 36 cc. of concentrated hydrochloric acid. The mixture was cooled to 2° C. and diazotised with 14 g. of sodium nitrite dissolved in 36 cc. of water. The diazonium salt was filtered through glass wool. The clear solution was poured into 52 cc. of borofluoric acid. (The acid was prepared by adding 1 mole equivalent of boric acid in small quantities into 4 mole equivalents of 48 per cent aqueous solution of hydrogen fluoride.) A white precipitate was formed which was filtered by suction, washed once with 30 cc. of borofluoric acid, twice with alcohol and twice with small amounts of ether. The diazonium salt was dried in vacuo over phosphorus pentoxide.

The dried bromo diazonium borofluoric acid was mixed with its weight of dried sand and placed in a 200 cc. distilling flask. The side arm of the flask was attached to a condenser, the latter was connected to a suction flask which served for a receiver, and this in turn was connected to a water suction pump. The flask was warmed gently; the decomposition of the diazonium salt started at about 130°. The fluorobromobenzene obtained was washed with dilute sodium hydroxide and distilled.

¹⁴F. C. Whitmore and R. J. Sobatzki, J. Am. Chem. Soc., 55, 1131 (1933).

¹⁵Balz and Schiemann, Ber., 60, 1186 (1927).

The boiling points of the products prepared and the yields obtained were as follows:

	B.P.	Yield %
Ortho-fluorobromobenzene	157-160°	37
Meta-fluorobromobenzene	148-151°	50
Para-fluorobromobenzene	150-152°	52

2. Preparation of Chlorobenzyl Bromide

The method used for the preparation of chlorobenzyl bromide consisted in treating chlorotoluene with bromine, using equimolal proportions of each. Fifty grams of bromine was added slowly to 39 g. of boiling chlorotoluene. The resulting product was washed with a ten per cent solution of sodium carbonate, and then with a water wash. The product was dried over anhydrous sodium sulfate and distilled. The yields and the boiling point of the resulting products were:

Compound	Yield %	B.P.
Ortho-chlorobenzyl bromide	72	103-104 @ 10 mm.
Meta-chlorobenzyl bromide	63	105-108 @ 8 mm.

3. Preparation of Meta-Bromophenyl Chloride

This product was prepared from meta-bromaniline. The bromaniline was diazotised and the diazonium salt decomposed with freshly prepared cuprous chloride. The yield was 72 per cent, B.Pt., 192°.

III. Preparation of Organo-Mercuric Compounds of the Type RHgX

Several methods were used for the preparation of the organo-mercuric compounds. The methods used are:

1. Sulfinic Acid Method.¹⁶

The benzensulfinic acid was made from aniline by the diazo reaction according to Gatterman's method.¹⁷ The sulfinic acid was boiled with three equivalents of mercuric acetate in glacial acetic acid, the solution filtered to remove the mercurous salts which are formed in the reaction, and the phenyl mercuric acetate precipitated from the solution by adding water or alkali. The phenyl mercuric chloride can be prepared by the addition of sodium chloride to aqueous or alcoholic solutions of the corresponding acetates.

The following is a detailed description of the preparation of para bromo mercuric chloride. By heating, in a 500 cc. Erlenmeyer flask, 10 g. of p-bromaniline is dissolved in a solution containing 44 cc. of concentrated sulfuric acid in 160 cc. of water. On cooling, white p-bromaniline sulfate crystallizes. The mixture is cooled well in ice, and 4.5 g. of sodium nitrite dissolved in 25 cc. of water is added gradually with constant mechanical stirring. After the nitrite has been added all the solid disappears. A well cooled solution of 22 cc. of concentrated sulfuric acid and 15 cc. of water is then added. The flasks and contents are weighed, and sulfur dioxide is passed in under pressure until the weight increase is 50 to 60 g. The speed of absorption of sulfur dioxide is greatly increased, when the flask is placed in a shaking machine and shaken continuously while the sulfur dioxide is passed into it. The mixture is then transferred to a 1000 cc. beaker immersed in a freezing mixture. About 50 g. of copper bronze is added gradually with constant stirring until the violent gas evolution is complete. During the addition of

¹⁶M. E. Hanke, J. Am. Chem. Soc., 45, 1321 (1923).

¹⁷Gatterman, Ber., 32, 1136 (1899).

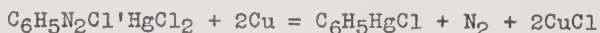
copper a slow stream of sulfur dioxide is passed through the liquid to insure an excess of this gas in solution. The p-bromobenzene sulfinic acid formed at this stage is practically insoluble.

The mixture is filtered and the residue, after being washed with a little water to remove excess of sulfuric acid, is extracted with 250 cc. of ten per cent sodium carbonate. The copper is removed by filtration. The filtrate is neutralized by cold fifty per cent sulfuric acid, and p-bromobenzene sulfinic acid separates as white glistening flakes.

The sulfinic acid is dissolved at once in 50 cc. of glacial acetic acid and a solution of 50 g. of mercuric acetate in 100 cc. of glacial acetic acid is added. A white precipitate of mercurous sulfinatate is formed at once. The mixture is heated to boiling for one hour, during which time the mercury salt of p-bromophenyl mercuric acetate is formed. This compound is very soluble in glacial acetic acid, while mercurous acetate and mercurous sulfate remain as solid. The mixture is filtered and the para bromophenyl mercuric acetate is precipitated from the filtrate by the addition of water. For the preparation of the p-bromophenyl mercuric chloride, each gram of the acetate was dissolved in 50 cc. of hot 75 per cent ethyl alcohol and 10 cc. of 10 per cent sodium chloride was added gradually while stirring. The chloride of the mercury compound was precipitated as a white crystalline solid.

2. Diazonium Mercuric Chloride Method¹⁸

The method consists in decomposing aryl diazonium mercuric chloride with catalytic copper, according to the reaction



¹⁸A. N. Nesmejanow, Ber., 62, 1010 (1929).

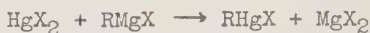
The following is the detailed description of the preparation of phenyl mercuric chloride as given by Nesmejanow.

To 23.5 g. of aniline placed in a beaker was added 100 cc. of concentrated hydrochloric acid. Three hundred cc. of water was added to the aniline hydrochloride. The beaker was immersed in ice. The aniline was diazotised with 18 g. of sodium nitrite dissolved in 20 cc. of water. The phenyl diazonium chloride formed was filtered, and to the filtrate was added 67.5 g. of mercuric chloride dissolved in a solution consisting of 70 cc. of water and 70 cc. of concentrated hydrochloric acid. A white precipitate of diazonium mercuric chloride was formed at once. The precipitate was washed with water, alcohol and ether. Each 10 g. of the salt was dissolved in 30-50 cc. of acetone, and to the solution was added 3 g. of electrolytic copper (2 moles). The mixture was stirred for 5-10 minutes. Evolution of nitrogen with liberation of heat was noticed. The mixture was allowed to stand for 12-24 hours. The acetone was then evaporated and the solid washed with ether to eliminate any products due to side reactions. The solid material was then extracted with the proper solvent using a Soxhlet extraction apparatus. The yield was 51 per cent.

By repeating exactly the procedure as described by Nesmejanow, it was found impossible to receive as high a yield of phenyl mercuric chloride as the author claimed to have obtained. Whenever the acetone solution of the diazonium salt was treated with catalytic copper, a tarry material was obtained from which it was difficult to extract the pure organo-mercuric halide. It was found of great use to substitute metallic mercury for copper in which case the decomposition of the diazonium salt was less vigorous, less tarry material was produced, and the yield of the organo-mercuric halide was higher.

3. Reaction of Mercuric Halide with a Grignard Reagent

The reaction occurs according to the equation



The procedure consisted in heating for one to two hours 1.2 mole of mercuric chloride with 1 mole of a Grignard reagent in ether solution. The product was then poured into water, the excess of mercuric chloride was dissolved, and the solid which consisted of organo-mercuric chloride was washed several times with water until no trace of mercuric chloride remained. (Tested with sodium hydroxide.) When the Grignard reagent used was of the type RMgBr , a mixture was sometimes formed consisting of organo-mercuric bromide and organo-mercuric chloride. Whenever this occurred, the organo-mercuric halide formed was shaken with freshly precipitated silver chloride.

a. Attempt to Prepare $\text{o-FC}_6\text{H}_4\text{HgCl}$

An attempt was made to prepare ortho-fluorophenyl mercuric chloride by reacting ortho-fluorophenyl magnesium bromide with mercuric chloride.

The first difficulty was encountered in preparing the Grignard reagent. Finally success was achieved in preparing ortho-fluorophenyl magnesium bromide by reacting 0.15 g. of magnesium with 1 g. of o-fluorophenyl bromide, dissolved in 10 cc. of anhydrous ether to which was added a small crystal of iodine. The reaction was carried out in a sealed tube at a temperature of 120° . The ether solution was decanted and reacted with an ether solution of mercuric chloride. A waxy material precipitated. The product was treated with water, and dilute sulfuric acid was added to dissolve the precipitated magnesium hydroxide. The waxy material was insoluble in ether and did not contain any

mercury (tested with stannous chloride). The ether solution, after being washed several times with water until test for mercuric chloride was negative, was evaporated; a gelatinous product remained. It was insoluble in both alcohol and petroleum ether. The test with stannous chloride showed the absence of mercury.

PROPERTIES OF THE ORGANO-MERCURIC COMPOUNDS (RHGX) PREPARED

Organo-Mercuric Compound Prepared	Method Used for Preparation	Starting Material Used for the Preparation of the Mercuric Compound	Yield %	Melting Point Degrees	Mercury Found %	Mercury Calculated %	Method of Analysis Used	Observation
C_6H_5HgCl	Modified Nesmejanow's method	$C_6H_5NH_2$	18	252	-	-	-	
$m-FC_6H_4HgCl$ ¹	$HgCl_2$ + Grignard reagent	$m-FC_6H_4Br$		243	58.8 58.9	60.4	Kharasch and Flenner	¹ The product obtained melted originally at 239°. After shaking it with freshly precipitated silver chloride the M.P. raised to 243°.
$p-FC_6H_4HgCl$	$HgCl_2$ + Grignard reagent	$p-FC_6H_4Br$		291	58.7 58.5	60.4	Kharasch and Flenner	
$p-ClC_6H_4HgCl$ ²	Nesmejanow's method	$p-ClC_6H_4NH_2$	25	238	57.1 57.2	57.8	Kharasch and Flenner	² Crystallized from hot alcohol
$o-BrC_6H_4HgCl$	Hanke's method	$o-BrC_6H_4NH_2$	44	155	-	-	-	
$o-BrC_6H_4HgCl$ ³	Nesmejanow's method	$o-BrC_6H_4NH_2$	0	-	-	-	-	³ Tarry product was obtained from which the $o-BrC_6H_4HgCl$ could not be recovered. Substituting ethanol for acetone did not improve the yield

PROPERTIES OF THE ORGANO-MERCURIC COMPOUNDS (RHGX) PREPARED (Continued)

Organo-Mercuric Compound Prepared	Method Used for Preparation	Starting Material Used for the Preparation of the Mercuric Compound	Yield %	Melting Point Degrees	Mercury Found %	Mercury Calculated %	Method of Analysis Used	Observation
⁴ m-BrC ₆ H ₄ HgCl	Hanke's method	m-BrC ₆ H ₄ NH ₂	50	194	-	-	-	⁴ Crystallized twice from alcohol
p-BrC ₆ H ₄ HgCl	Hanke's method	p-BrC ₆ H ₄ NH ₂	60	250	-	-	-	
p-BrC ₆ H ₄ HgCl	Nesmejanow's method	p-BrC ₆ H ₄ NH ₂	28	248	-	-	-	
p-BrC ₆ H ₄ HgCl	Modified Nesmejanow's method	p-BrC ₆ H ₄ NH ₂	55	255	-	-	-	
⁵ m-CF ₃ C ₆ H ₄ HgCl	Modified Nesmejanow's method	m-CF ₃ C ₆ H ₄ NH ₂	20	151	53.22	52.63	Electrometric	⁵ Crystallized from hot alcohol
C ₆ H ₅ CH ₂ HgCl	HgCl ₂ + Grignard reagent	C ₆ H ₅ CH ₂ Cl	74	107	-	-	-	
o-ClC ₆ H ₄ CH ₂ HgCl	HgCl ₂ + Grignard reagent	ClC ₆ H ₄ CH ₂ Cl	25	115	-	-	-	
m-ClC ₆ H ₄ CH ₂ HgCl	HgCl ₂ + Grignard reagent	m-ClC ₆ H ₄ CH ₂ Br	40	141	54.8 54.8	55.4	Whitmore and Sobatzsky	
p-ClC ₆ H ₄ CH ₂ HgCl	HgCl ₂ + Grignard reagent	p-ClC ₆ H ₄ CH ₂ Br	55	141	-	-	-	

IV. Preparation of Unsymmetrical Mercury Compound

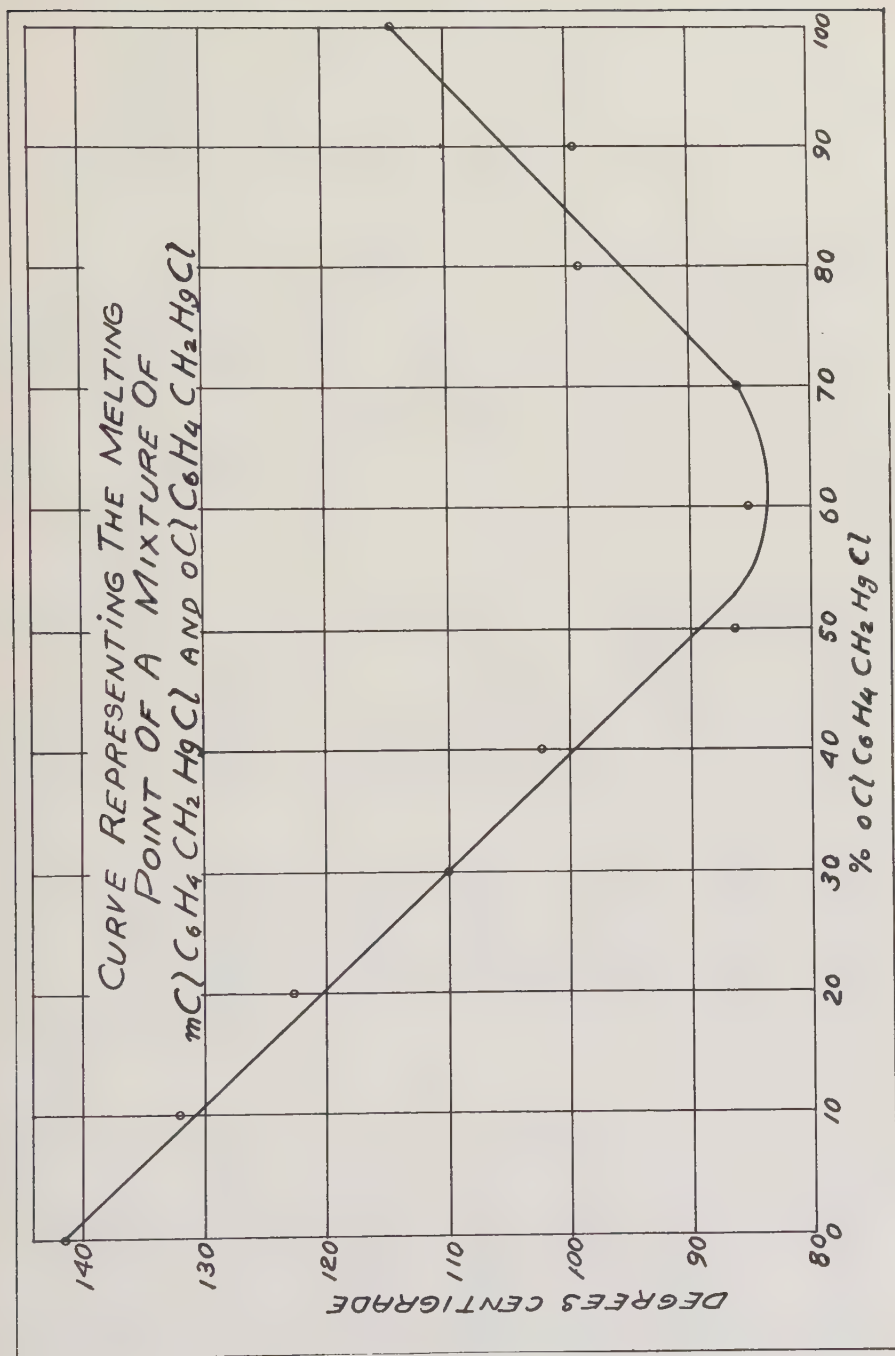
About 5 g. of the organo-mercuric chloride was added in small portions at a time to about two molecular equivalents of the Grignard reagent of the other radical in anhydrous ethyl ether. The mixture was shaken constantly and kept immersed in ice water during the addition. After all the mercury compound had been added, the mixture was shaken until all of the solid dissolved.



The excess Grignard reagent was then decomposed by ice and ten per cent solution of sulfuric acid, care being taken that the temperature does not rise about 10°. The unsymmetrical organo-mercuric compound was extracted with ether and dried with anhydrous sodium sulfate. It was then filtered, and the ether evaporated in vacuo. The product thus obtained was washed several times with anhydrous alcohol and dried in vacuo. The melting point and the percentage of mercury was determined.

To about 1.2 g. of the foregoing product, dissolved in ethyl ether, about 4 cc. of saturated solution of hydrogen chloride in alcohol was added. The product was warmed slightly for about five minutes and the solution evaporated. The solid product obtained was then crystallized from a small amount of alcohol. The melting point and the mercury content of this compound was determined.

To another 1.2 g. portion of the unsymmetrical mercury compound in ether a molecular equivalent of mercuric chloride was added. The mixture was refluxed for ten minutes, evaporated and the products separated and purified by the use of suitable solvents. The melting point and the mercury content of this product was determined and found to be:



PROPERTIES OF THE UNSYMMETRICAL MERCURY COMPOUNDS (Continued)

Compound	Method of Preparation	M.P.	Mercury Analysis			Cleavage with HCl	
			Method	Hg % Found	Hg % Calculated	M.P.	Mercury Analysis Method
m-BrC ₆ H ₄ HgC ₆ H ₅	C ₆ H ₅ MgBr + m-BrC ₆ H ₄ HgCl	Liquid	Kharasch and Flenner	45.15	46.1	183-186°	Analysis
							Hg % Found
p-BrC ₆ H ₄ HgC ₆ H ₅	C ₆ H ₅ MgBr + p-BrC ₆ H ₄ HgCl	151-175°	Kharasch and Flenner	46.2	46.1	238°	Composition of the Decomposed Compound
				46.5			
p-BrC ₆ H ₄ HgC ₆ H ₅	C ₆ H ₅ MgBr + p-BrC ₆ H ₄ HgCl	136-176°	-	-	-	233-235°	
m-CF ₃ C ₆ H ₄ HgC ₆ H ₅	C ₆ H ₅ MgBr + m-CF ₃ C ₆ H ₄ HgCl	100-103°	Electroanalysis	47.4	47.8	159-160°	
m-CF ₃ C ₆ H ₄ HgC ₆ H ₄ Cl _m	m-ClC ₆ H ₄ MgBr + m-CF ₃ C ₆ H ₄ HgCl	130-143°	Elect.	44.0	43.6	164°	
m-CF ₃ C ₆ H ₄ HgC ₆ H ₄ Cl _m	m-ClC ₆ H ₄ MgBr + m-CF ₃ C ₆ H ₄ HgCl	130-140°	Whitmore and So-batzsky	43.5	43.6	159-163°	
				43.7			
m-CF ₃ C ₆ H ₄ HgC ₆ H ₄ Cl _m	m-ClC ₆ H ₄ MgBr + m-CF ₃ C ₆ H ₄ HgCl	130-139°	-	-	-	164-166°	
o-ClC ₆ H ₄ CH ₂ HgCH ₂ C ₆ H ₄ Cl _m ^a	m-ClC ₆ M ₄ CH ₂ MgBr + o-ClC ₆ H ₄ CH ₂ HgCl	Liquid	Whitmore and So-batzsky	42.8	44.3	87° ^b	
				42.9			

^a^b

PROPERTIES OF THE UNSYMMETRICAL MERCURY COMPOUNDS (Continued)

Compound	Method of Preparation	M.P.	Mercury Analysis		Cleavage with HCl			Composition of the Decomposed Compound
			Method	Hg % Found	Hg % Calculated	M.P.	Mercury Analysis	
							Method	
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{ClO}$	$o\text{-ClC}_6\text{H}_4\text{CH}_2\text{MgBr} + p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCl}$	90-113°	Whitmore and So-batzsky	43.9	44.3	-	-	-
$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCH}_2\text{C}_6\text{H}_4\text{ClO}^a$	$o\text{-ClC}_6\text{H}_4\text{CH}_2\text{MgBr} + p\text{-ClC}_6\text{H}_4\text{CH}_2\text{HgCl}$	98-129°	-	-	-	99° ^c 110° and So-batzsky	54.9	-
$\text{C}_6\text{H}_5\text{HgC}_2\text{H}_5^d$	$\text{C}_6\text{H}_5\text{MgBr} + \text{C}_2\text{H}_5\text{HgCl}$	Liquid	-	-	-	-	-	-

^aThe unsymmetrical compound was very stable and could not be decomposed with alcoholic hydrogen chloride at room temperature. The decomposition was effected by heating the reagents at 60° for twenty minutes.

^bThe melting point corresponds to a mixture of ortho and meta chlorbenzyl mercury chloride. A melting point curve of a synthetic mixture of the two compounds was made (see attached curve). As seen from the curve, melting point of 87° corresponds to a mixture consisting of 50-70 per cent of ortho chlorbenzyl mercury chloride, the remainder being meta chlorbenzyl mercury chloride. By adding 10 per cent of meta chlorbenzyl mercury chloride to the hydrogen chloride split, the melting point of the split rose to 100°, which indicates that the split consisted of equimolal proportions of ortho and meta chlorbenzyl chlorides.

^cThe split consists of a mixture of ortho and para chlorbenzyl mercury chlorides.

^dThe unsymmetrical mercury compound was treated with hydrogen bromide, chloride and iodide. The experimental results are given in the following chapter.

DECOMPOSITION OF $C_6H_5HgC_2H_5$ WITH HYDROGEN HALIDES

The phenyl mercury ethyl was decomposed with hydrogen chloride, hydrogen bromide and hydrogen iodide in different solvents.

1. Hydrogen Chloride

Mercury phenyl ethyl (1.3 g.) was dissolved in 25-30 cc. of ethanol and to this was added 7 cc. of ethanol saturated with hydrogen chloride. A solid which separated after filtering and washing with ether melted at 192° .

2. Hydrogen Bromide

a. Benzene

Mercury phenyl ethyl (1.5 g.) was dissolved in 25-30 cc. of benzene. To this solution, kept at 15° , was added 15 cc. of benzene saturated with hydrogen bromide. A gelatinous precipitate was formed at once, but on stirring brown leaflets deposited. Some of the benzene was evaporated by passing over the solution a stream of air. The solid was separated by filtration, washed with petroleum ether and ethyl ether. White leaflets were obtained which melted at 189° .

b. Glacial Acetic Acid

One gram of mercury phenyl ethyl was dissolved in 20 cc. of glacial acetic acid. To this was added 7-10 cc. of glacial acetic saturated with hydrogen bromide. A precipitate was formed, which was filtered and washed with petroleum ether. The crystals soften at 187° and melt at 189° .

c. Ethanol

The procedure was the same as in (b), 7 cc. of ethanol saturated with hydrogen bromide being added. The crystals soften

at 187° and melt at 189°.

3. Hydrogen Iodide

The hydrogen iodide was prepared by reacting glacial phosphoric acid with sodium iodide.

a. Benzene

Gaseous hydrogen iodide was passed into a benzene solution containing one to 1.3 g. of mercury phenyl ethyl. A reddish precipitate formed. Part of the benzene was evaporated by a stream of air and the precipitate was filtered. It sublimed at 215° C., probably due to some mercuric iodide which could have been formed by side reactions. The precipitate was extracted with acetone, filtered, and the acetone evaporated. A white product of an unpleasant odor was obtained which softened at 162° and melted at 175° C.

b. Glacial Acetic Acid

The procedure used was similar to the one described above. A white crystalline product was obtained which softened at 179° and melted at 181°.

SUMMARY

The electronegativities of meta and para-fluorophenyl, para-chlorophenyl, ortho, meta and para bromophenyl radicals were compared with phenyl radical.

The order of electronegativities of ortho, meta and para chlorobenzyis was determined.

The electronegativity of the meta-1,1,1 trifluorotolyl radical was compared with that of phenyl and metachlorophenyl radical.

It was shown that the variation in solvent and hydrolytic agent has no effect upon the order of electropositivity of organic radicals.

ACKNOWLEDGMENT

I wish to express my sincerest appreciation to Professor M. S. Zharasch for his guidance and instruction.

